(19) JAPANESE PATENT OFFICE

PATENT ABSTRACTS OF JAPAN

(11) Publication number: **08278199 A**

(43) Date of publication of application: **22.10.96**

(51) Int. Cl **G01J 3/02**
G01J 3/45
G01N 21/27

(21) Application number: **07129866**

(22) Date of filing: **03.04.95**

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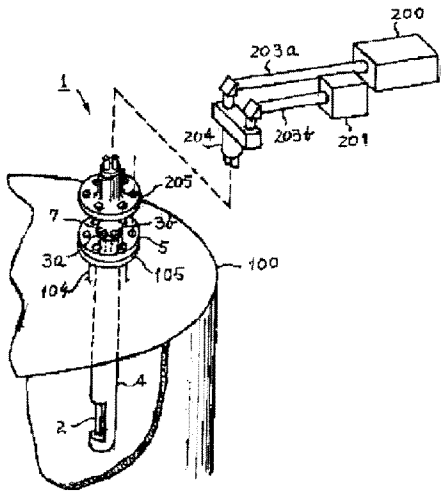
(54) INFRARED PROBE DEVICE

(57) Abstract:

PURPOSE: To provide a safely structured probe which can surely prevent gas from being blown out to those of FT-IR and outside of system even if an ATR cell is broken down.

CONSTITUTION: This probe device is provided with a probe 4 holding two internal optical passes 3a and 3b, holding an infrared ATR cell 2 being dipped in a reaction solution in a high pressure autoclave at its thp part, and installing a mounting flange 5 to the autoclave at the other end, and optically connecting an interval between the ATR cell 2 and the other end, and a pressure-proof window member 7 passing through infrared rays at low loss while resistible to the working pressure of the autoclave, respectively. In a state that the prove 4 is inserted into the autoclave, the pressure-proof window member 7 is superposed on a probe flange 5 and it is airtightly clamped to a nozzle of an autoclave vessel wall, the FT-IR at the outside of the autoclave and a detector and these optical passes 3a and 3b in an inner part of the probe 4 are optically connected together via the pressure-proof window member 7.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to the infrared probe device for holding an infrared ATR cell safely in high voltage autoclave.
[0002]
[Description of the Prior Art]Although an infrared ATR (Attenuated Total Reflection) cell is low sensitivity compared with the conventional transmission type cell, it has the outstanding feature that a cell can be immersed in reaction mixture and an infrared absorption spectrum can be obtained to in-situ. And by development of a computer in recent years the S/N ratio of the weak absorption-spectrum signal under ATR cell output, As a result of improving substantially by using the mathematical technique of the Fourier transform and inverse transformation, the weak point of an ATR method called low sensitivity is conquered as a matter of fact, and is establishing the status as the quantitative-analysis technique.
[0003]Generally, the infrared spectral device using such the Fourier transform is called FT-IR (Fourier Transform Infrared Spectrometer).
[0004]In FT-IR according to an ATR method to one analysis taking several minutes at the infrared spectroscopy by the conventional transmission type cell, several repetitive analysis is possible in 1 second, and it is very quick.
[0005]If the above-mentioned feature of an ATR method can be harnessed, it will become possible to pursue an on-going reaction process in real time, and to perform useful processings, such as reaction control. However, in order to put an ATR method in practical use under the harsh-environment conditions which encounter by actual chemicals article manufacturing processes, such as an elevated temperature, high voltage, hyperviscosity, and ignition explosivility, there are many problems which should still be solved.
[0006]The artificers of this invention considered application of the ATR method, in order to determine the hydrogenation reaction cancel stage in the manufacturing process of the high saturation type compound by a hydrogenation reaction (henceforth a "hydrogenation reaction"). That is, concentration, such as a C=C double bond in the solution cement which

dissolved the compound which has an unsaturated bond in the solvent, tends to be pursued in real time by ATR method FT-IR, and it is going to judge whether the target hydrogenation rate was reached.

[0007]For that purpose, although it is necessary to establish the analytical curve which can presume a hydrogenation rate in necessary accuracy by making into an explaining variable the extinction quotient of the various intramolecular structural sites obtained from the infrared absorption spectrum at hydrogenation reaction temperature of course, it increases also to it and reservation of safety is important.

[0008]At a hydrogenation process, in order that disclosure nature and explosivility may treat very high hydrogen in large quantities and may raise reaction velocity, hydrogen is supplied to autoclave with high voltage. And an ATR cell is arranged in the autoclave full of hydrogen.

[0009]Usually, although an ATR cell is protected and used with a probe, the necessity of touching the reaction mixture in autoclave directly to the part has exposed the cell from the probe. When a crevice is made from such a structure at the case where a cell is damaged by a certain cause, a cell, and the joint of a probe, the contents of autoclave invade into a probe and may reach even out of FT-IR or a system through the optical path of pipe shape. There are a hot infrared lamp, a relay contact, etc. in FT-IR, and it becomes an ignition source when hydrogen gas invades.

[0010]

[Problem(s) to be Solved by the Invention]Therefore, in the probe of an ATR method, even if a cell is damaged, the technical problem of this invention, It is providing the probe of a safe structure which can prevent gas from spouting out of FT-IR or a system from portions, such as an optical path, certainly, and infrared light's can moreover go back and forth between FT-IR and ATR cells freely, and does not interfere with observation of an infrared absorption spectrum.

[0011]

[Means for Solving the Problem]The above-mentioned technical problem holds an infrared ATR cell immersed in reaction mixture in high voltage autoclave to the tip part, A probe which holds in one an internal optical path which equips the other end with an airtight mounting means to autoclave, and connects between an ATR cell and said other ends optically to the inside with said ATR cell, Where it passed infrared light by low-loss, and it had a pressure-tight-window member which can bear a working pressure range of autoclave and said probe is inserted into autoclave, Said pressure-tight-window member is airtightly fixed to a mounting means of said probe in a mounting hole of an autoclave container wall in piles, It is attained by infrared probe device of this invention connecting optically an infrared device besides autoclave, and an optical path inside said probe via said pressure-tight-window member.

[0012]Said pressure-tight-window member in the above-mentioned infrared probe device can consist of KRS-5 material of specified shape. KRS-5 is a crystal of a thallium bromide

thallium iodide mixture, and it has the characteristic which it not only excels as an optical material, but can be hard to break strongly [a shock]. However, if it is the material which has the performance in alignment with a business solution principle of this invention even if it is other materials, it cannot be overemphasized that it is not necessarily restricted to KRS-5 material. For example, KRS-6 which is a thallium bromide thallium chloride mixture can also be used.

[0013]The above-mentioned infrared probe device can be further provided with a cutoff valve which can intercept said internal optical path.

[0014]The above-mentioned cutoff valve can be a ball valve or a lubricated plug valve which has two parallel breakthroughs in a valve element.

[0015]

[Function]Though an ATR cell is held at a probe and the probe itself has a certain amount of resistance to pressure, the necessity of touching the reaction mixture in autoclave directly to the part has exposed the cell from the probe. When a cell is damaged by a certain cause or a crevice is made from such a structure at a cell and the joint of a probe, the contents of autoclave may invade into a probe.

[0016]However, in the infrared probe device of this invention, pass infrared light by low-loss, and provide the pressure tight window which consists of a pressure-tight-window member which can bear the working pressure range of autoclave in the container wall of autoclave, and it borders on this pressure tight window, The whole probe holding an ATR cell and its required accessories is shut up into the high voltage zone of autoclave. Therefore, they are prevented from spouting to an external low-pressure zone, even if an ATR cell should be damaged and reaction mixture and hydrogen gas should invade into a probe.

[0017]Since the infrared light can go back and forth between FT-IR of an ATR cell and the exterior freely by low-loss through said pressure tight window, the above-mentioned infrared probe device does not become the hindrance of observation of an infrared absorption spectrum.

[0018]Thus, in the infrared probe device of this invention, pressure-tight-window members are major parts which hold the key of the success or failure of an invention.

[0019]The artificers of this invention found out that the optical material called KRS-5 which is acknowledged from the former in infrared permeation performance had the performance outstanding also in the mechanical strength, as a result of testing various kinds of materials. The board of the KRS-5 material of prescribed thickness confirmed experimentally that it could fully bear, even when the internal pressure of autoclave was applied to step form at a stretch. The thickness of a pressure-tight-window member is Mechanical Engineer's Handbook, 4th Ed., McGrow Hill Book Co., and Inc. The following formula of printing can determine.

[0020]t/D=0.866(P/Fa)1/2 -- here, it is a diameter (mm) of the elasticity limit (kg/cm2) of t:thickness (mm) Fa:appearance, P:pressure (kg/cm2), and D:circular shape.

[0021]In this invention, providing a cutoff valve in the middle of the internal optical path of a probe has a meaning of double-izing of safety measures. That is, although this valve is usually opened, when it is detected that a probe has leakage, this is stopped promptly. Thereby, a pressure tight window can be protected from the shock pressure by breakage of a cell, etc. When it is discovered that a pressure tight window has a certain problem, even if it is during operation of autoclave, by closing a cutoff valve, check and clearing work can be performed safely and safety can be improved further.
[0022]Although the ball valve or lubricated plug valve which can be operated quick is preferred as a valve form of a cutoff valve, there is only one channel hole with the usual valve. Since in the case of this invention it is necessary to classify two optical paths so that the infrared light of a round trip may not be mixed, two valves must be used. However, it is inconvenient to become what then cannot disregard ****** of a cutoff valve, and to carry out the emergency trip of the two optical paths by one operation. Then, the ball valve or lubricated plug valve which has two parallel breakthroughs in a valve element was made to prepare specially because of the infrared probe device of this invention.
[0023]
[Example]Before starting explanation of an example, it surveys about the structure and the working principle of the entire configuration of the hydrogenation reactor with which the infrared probe device of this invention is used, and the ATR cell.
[0024](Entire configuration of a hydrogenation reactor) Drawing 1 is a block diagram showing an example of a hydrogenation reactor. The reactor of the center of a drawing is the autoclave 100 with the jacket for cooling, and an agitator, solution cement and the hydrogenation reaction catalyst of the compound which have an unsaturated bond in this are charged, and hydrogen gas is continuously supplied through the flow instrument 101, stirring with an agitator. The temperature in autoclave is controlled by the temperature controller 102, and cooling water is supplied to a jacket according to the calorific value inside autoclave.
[0025]In this reaction apparatus, the infrared probe device 1 of this invention is inserted from the upper part of the autoclave 100. Infrared light is supplied to the ATR cell 2 in autoclave through the optical path 203a, and returns from FT-IR200 currently installed out of the autoclave 100 to the detector 201 besides the autoclave 100 through the cell 2 to the optical path 203b.
[0026]The output signal of the ATR cell 2 detected with the detector 201 is supplied to FT-IR200, signal processing is carried out here, and an absorption spectrum is extracted. An absorption-spectrum signal is inputted to another computer 202, and presumption of a hydrogenation rate is performed. Presumed hydrogenation rate data is sent to the autoclave control device which is not illustrated, and required control actions, such as a reaction stop, are performed.
[0027]Since it is necessary to install FT-IR200 and the detector 201 near the autoclave 100, it accommodates in the internal pressure explosion protection box which carried out

nitrogen application of pressure, and contact with combustible gas is prevented. Computer 202 and others are installed in the non-explosion protection zone distant from the autoclave 100.

[0028]When the ATR cell 2 is immersed in hyperviscous solution cement, we are anxious about the sensitivity lowering by the dirt of the cell 2, but in the case of the hydrogenation process which uses the infrared probe device of this invention, if about one cleaning is performed in tens batches, it will have become clear that it is satisfactory practically.

[0029](The structure and the working principle of an ATR cell) Drawing 2 is a sectional view showing the structure of an ATR cell.

[0030]From the probe 4, a rod is exposed to the hollow 6 of the lower end part of the probe 4 of the ATR cell 2, and is held at it. Since this rod is a main part of the ATR cell 2, it attaches the same numerals 2 as a cell in the following explanation. The rod 2 consists of an optical material ground by square pole form, and this portion carries out direct contact to the reaction mixture which is a measuring object. It is connected to the upper bed of the rod 2, and the lower end of the optical path 3a will give the incident light which goes for the bottoms of slant from the both sides of the rod 2, if it turns caudad from the optical path 3a and infrared light enters. It is ejected from the other end, infrared light carrying out total internal reflection of the inside of the rod 2 many times.

[0031]When infrared light carries out total internal reflection in the rod 2, the light of a **** minute amount oozes out into reaction mixture across the interface of the rod 2, the light of a wave number (wavelength) peculiar to the atom group who encounters there is absorbed, and the light which remained returns into the rod 2 again.

[0032]Therefore, since all of incident light are not reflected as for total internal reflection but the light in which only the part by which the luminous intensity of the absorption wave number was absorbed decreased is reflected, an absorption spectrum will be contained in the exit light from the rod 2. However, since most incident light turns into catoptric light as it is and an absorption spectrum only accounts for very few rates of catoptric light, the sensitivity of the ATR cell 2 to absorption is low. Then, absorption sensitivity is raised by if possible repeating total internal reflection in the rod 2 many times, and the work which raises a S/N ratio in a signal-processing stage is carried out as mentioned above.

[0033]The course is changed by 180 degrees in the lower end of a probe, and the infrared light ejected from the rod 2 follows the inside of the optical path 3b by the side of figure Nakamigi upwards, and results in the detector 201.

[0034]One example of (explanation of an example), next this invention is described. Drawing 3 is a perspective view including the partial perspective diagram of the infrared probe device 1 in this example. This infrared probe device 1 is inserted from the upper part of the autoclave 100 like what was shown in above-mentioned drawing 1. The external optical paths 203a and 203b which tie these and the infrared probe device 1 with FT-IR200 besides the infrared probe device 1 and the detector 201 are shown in drawing 3.

[0035]The probe 4 makes a cylindrical shape and it has the flange 5 in the upper bed, and it

is held where the rod 2 is exposed to the lower part of the probe 4. Inside the probe 4, the internal optical paths 3a and 3b of two are prolonged from the rod 2 to the height of the flange face of probe 4 upper bed.

[0036]The nozzle 104 with the flange 105 as some high pressure vessels is welded to the panel of the autoclave 100 upper part.

The probe 4 is inserted from here.

The flanges 5 and 105 of the probe 4 and the nozzle 104 are doubled, and the packing material is made to intervene between them in that case. On the flange 5 of the probe 4, on both sides of the disk 7 of the KRS-5 material ground in the predetermined diameter and thickness which can bear the working pressure of autoclave, put on the packing material of two sheets, and further Next, the top to the probe 4, The external optical path 203a which connects FT-IR200 and the detector 201, The internal and external optical paths 3a and 203a and the optic axis of 3b and 203b are set, and the flange 205 of the pipe 204 loaded with 203b is carried, and above, a bolt fastens the flanges 5, 105, and 205 of three sheets, and it sticks, and fixes. In this way, the infrared probe device 1 of this example is completed.

[0037]Below, an operation of the infrared probe device 1 of this example is explained.

[0038]Even though the rod 2 is held at the probe 4 and probe 4 the very thing has a certain amount of resistance to pressure, the reaction mixture in the autoclave 100 is touched directly, and also [required] the part has exposed the rod 2 from the probe 4. When the rod 2 is damaged by a certain cause or a crevice is made from such a structure at the rod 2 and the joint of the probe 4, the contents of the autoclave 100 may invade into the probe 4.

[0039]However, the pressure tight window 7 which infrared light is passed by low-loss, and consists of a disk of KRS-5 material which can bear the working pressure range of autoclave in the probe device 1 of this example, It fixed on the flanged nozzle 104 as some high pressure vessels, and the probe 4 whole is shut up in the high voltage zone of the autoclave 100 bordering on this pressure tight window 7. Therefore, even if the rod 2 should be damaged and reaction mixture and hydrogen gas should invade into the probe 4, they are beforehand prevented from spouting to an external low-pressure zone.

[0040]Since the infrared light can go back and forth between FT-IR200 of the rod 2 and the exterior, and the detectors 201 freely by low-loss through the pressure tight window 7, the above-mentioned infrared probe device 1 does not give trouble to observation of an infrared absorption spectrum.

[0041]The infrared probe device 1 of the type inserted from the upper part of the autoclave 100 explained in the top fits the use with a short distance from the panel of autoclave to a contents oil level with comparatively small autoclave. With large-sized autoclave, since the distance to said oil level is long, with the infrared probe device of a top inserting type, the overall length of the probe 4 must be lengthened, therefore there is inconvenience, like the probe 4 vibrates easily.

[0042]Other examples of (explanation of other examples), next this invention are described.

Drawing 4 is drawing of longitudinal section of the infrared probe device 10 of this example. Unlike what was shown in above-mentioned drawing 3, the infrared probe device 10 of this example is inserted from the pars basilaris ossis occipitalis of the autoclave 100. It has the advantage that this type of infrared probe device 10 can shorten an overall length, and the infrared probe device 10 of the pars-basilaris-ossis-occipitalis inserting type is especially suitable for the reason mentioned above with the large-sized autoclave 100.

[0043]The point that this example differs from the example of drawing 3 in addition to it is having the cutoff valve 8 and the nozzle 9 for pressure detection between the flange 5 of the probe 4, and the pressure tight window 7. The pressure sensor which is not illustrated is connected to the nozzle 9. The cutoff valve 8 is 2 hole ball valve. This valve 8 is usually opened and two parallel breakthroughs provided in the valve element are functioning as some internal optical paths 3a and 3b of a round trip. However, when it is detected that the probe 4 has leakage with the pressure sensor linked to the nozzle 9, it is stopped promptly.

[0044]These can be prevented from intercepting contents and hydrogen gas of the autoclave 100 which invaded into the probe 4 by breakage of the rod 2, etc., and exerting impulse force on the pressure tight window 7 by having formed the cutoff valve 8. When the pressure tight window 7 has a certain problem, even if it is during operation of the autoclave 100, check and clearing work can be safely performed by closing the cutoff valve 8. Therefore, safety can be improved further.

[0045]Also in this example, since the point and others which have shut up the probe 4 whole in the high voltage zone of the autoclave 100 bordering on the pressure tight window 7 are the same as the example of above-mentioned drawing 3, they omit detailed explanation of the operation.

[0046](Explanation of a pressure-tight-window material testing apparatus) Drawing 5 is a figure showing the composition of the device which examines the pressure-tight-window material used for the infrared probe device of this invention. It is a device which fixes the disk created with the material examined by the flange at the tip of piping, makes the water of sand mixture collide aiming at this disk, and gives a shock pressure. In this case, sand is imitating the smashed fragment of a rod and sign RD in a figure expresses the rupture disk which explodes in specified pressure.

[0047]It checked having a mechanical strength which the disk of the KRS-5 material ground in predetermined thickness can use for this invention using this test equipment.

[0048]

[Effect of the Invention]In the infrared probe device of this invention, pass infrared light by low-loss, and provide the pressure tight window which consists of a pressure-tight-window member which can bear the working pressure range of high voltage autoclave in the container wall of autoclave, and it borders on this pressure tight window, The whole probe holding an ATR cell and its required accessories is shut up into the high voltage zone of autoclave. Therefore, they are prevented from spouting to an external low-pressure zone, even if an ATR cell should be damaged and reaction mixture and hydrogen gas should

invade into a probe.

[0049]Since the infrared light can go back and forth between FT-IR of an ATR cell and the exterior freely by low-loss through said pressure tight window, the above-mentioned infrared probe device does not become the hindrance of observation of an infrared absorption spectrum.

[0050]Therefore, with the infrared probe device of this invention, an infrared ATR cell can be held safely in high voltage autoclave, and the performance of an infrared ATR cell can be demonstrated perfectly. By using this device, concentration, such as a C=C double bond in solution cement, is pursued in real time by ATR method FT-IR, and it becomes possible to judge whether the target hydrogenation rate was reached.

[0051]The infrared probe device of this invention can be used for the hydrogenation reaction of an unsaturation low molecular weight compound, etc. at the hydrogenation reaction of unsaturation type polymers, such as SBR, a styrene butadiene block copolymer, a styrene isoprene block copolymer, NBR, poly norbornene, and petroleum resin, and a pan.

[0052]

[Translation done.]

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CLAIMS

[Claim(s)]
[Claim 1]Where it had the following and said probe is inserted into autoclave, An infrared probe device which fixes said pressure-tight-window member to a mounting means of said probe airtightly in a mounting hole of an autoclave container wall in piles, and is characterized by connecting optically an infrared device besides autoclave, and an optical path inside said probe via said pressure-tight-window member.
A probe which holds in one an internal optical path which holds an infrared ATR cell immersed in reaction mixture in high voltage autoclave to the tip part, equips the other end with an airtight mounting means to autoclave, and connects between an ATR cell and said other ends optically to the inside with said ATR cell.
A pressure-tight-window member which infrared light is passed by low-loss, and can bear a working pressure range of autoclave.

[Translation done.]